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Title: Chemistry and refractory grain formation in Fireballs

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Chemistry and refractory grain formation in Fireballs

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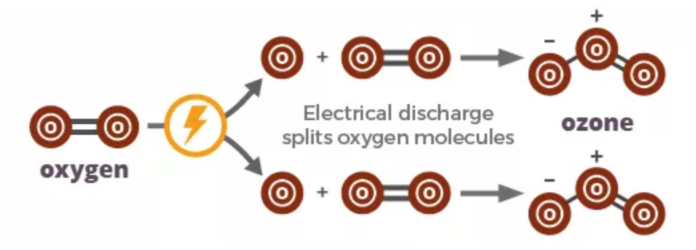
Overview

Modelling of near-field chemistry and nucleation efficiency of refractory dust grains (nanometer-sized molecules in the solid phase).

- Description of low-altitude air chemistry and dust
- Model overview
- Nucleation, chemical network, and surface chemistry
- Coupling to hydrodynamics
- Recent results
- Observational opportunities
- Conclusion and outlook

Chemical compounds and particulate matter formation in flash-heating air



Vaporization and recombination of air leads to local enhancement of ozone, nitrates, and carbon-bearing compounds

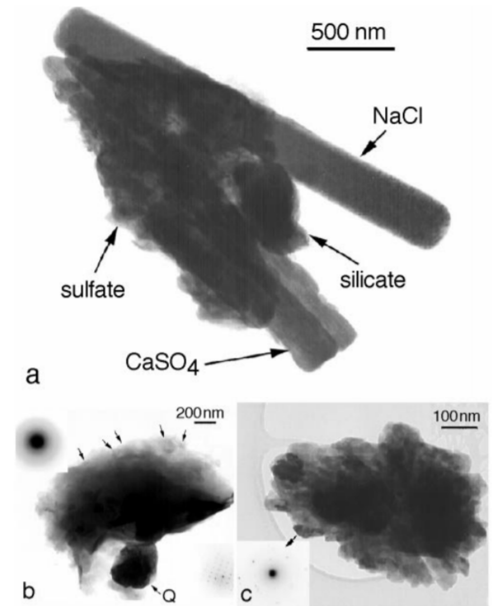
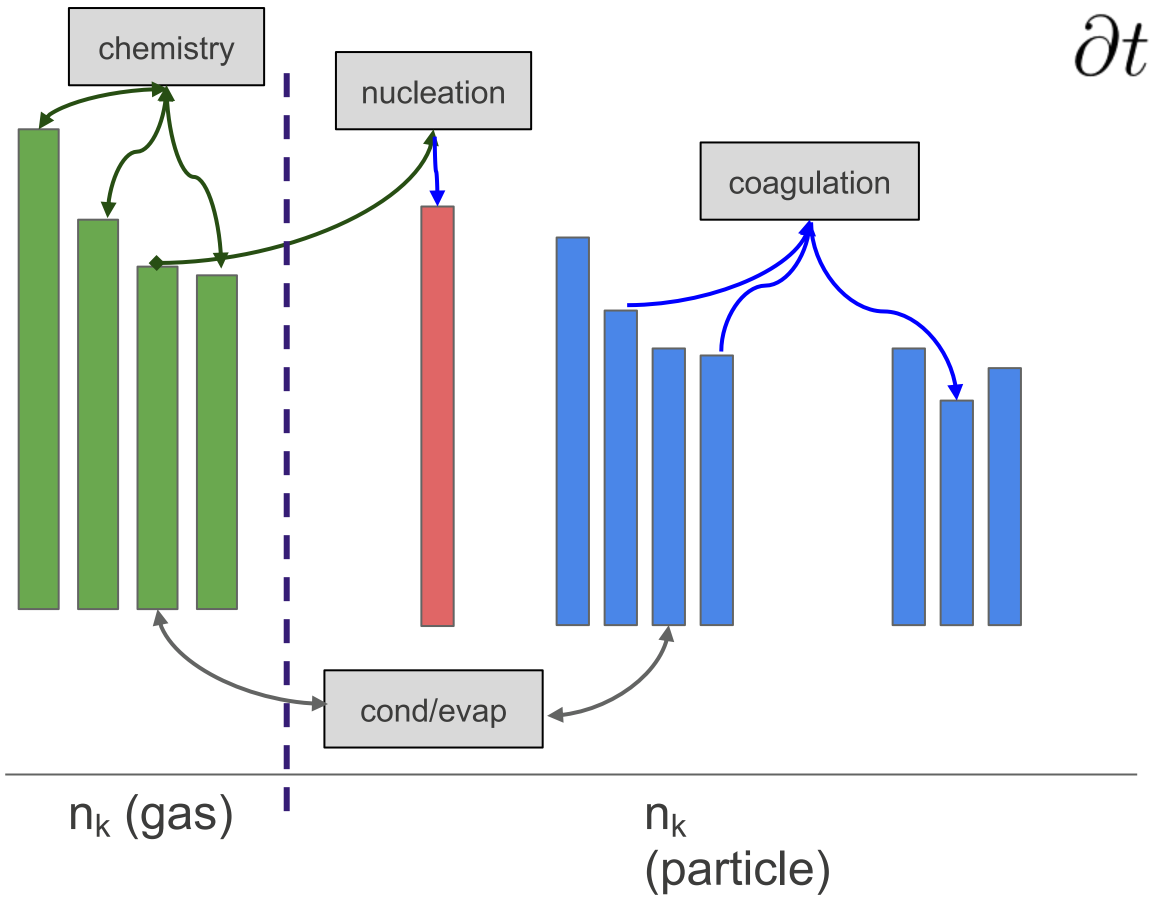


FIG. 7. TEM images of mineral dust collected from the marine troposphere. (*a*) Internal mixture of presumably terrestrial silicate and anhydrite with sea salt (Azores, North Atlantic, ASTEX/MAGE); (*b*) smectite (clay) and quartz (Q). The small grain size of the clay is visible at the thin edge (the arrows mark hexagonal platelets). Selected-area electron-diffraction patterns of clay and quartz are at the upper left and lower right, respectively. (Canary Islands, North Atlantic, ACE-2); (*c*) TEM image of goethite, FeO(OH), collected 2,600 m above sea level. Fe-bearing minerals like this could be important nutrient sources in remote oceans. (Canary Islands, North Atlantic, ACE-2.)

Buseck & Posfai, 1999

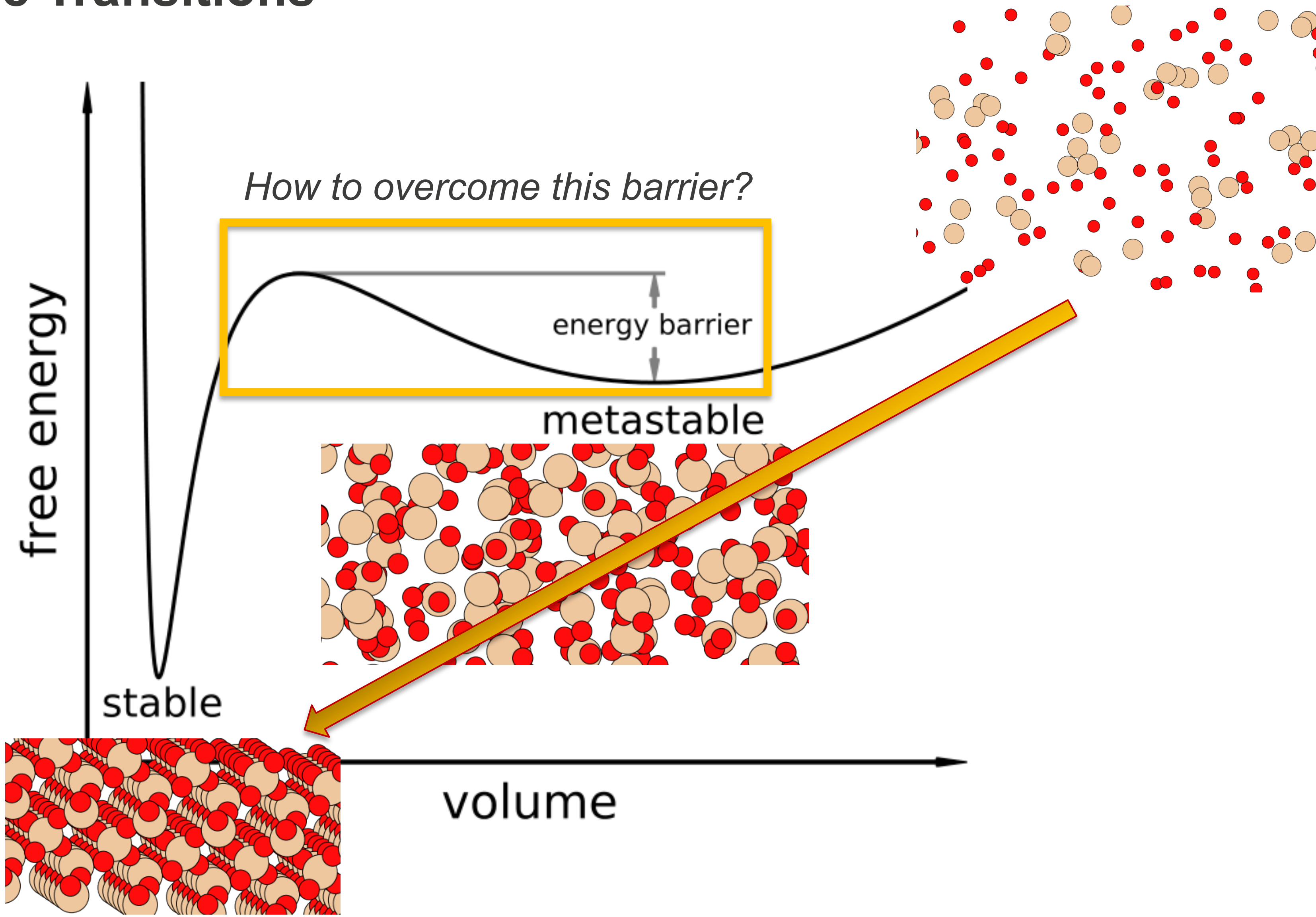
Dust and aerosol particles condense from vapor, and provide a cite for gas-phase chemical processing and seeding for additional dust production

Dust/aerosol and chemistry self-consistent model



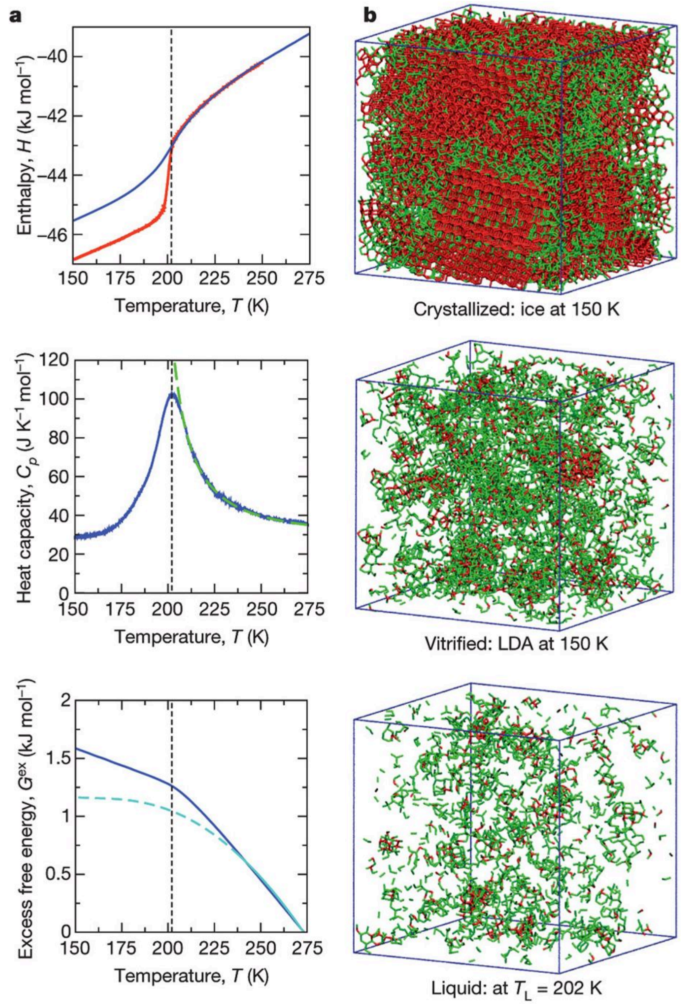
$$\frac{\partial n_k}{\partial t} = \left[\frac{\partial n_k}{\partial t}\right]_{cond,evap} + \left[\frac{\partial n_k}{\partial t}\right]_{nucl} + \left[\frac{\partial n_k}{\partial t}\right]_{chem} + \left[\frac{\partial n_k}{\partial t}\right]_{coag}$$

Phase Transitions



Phase transitions, metastable matter

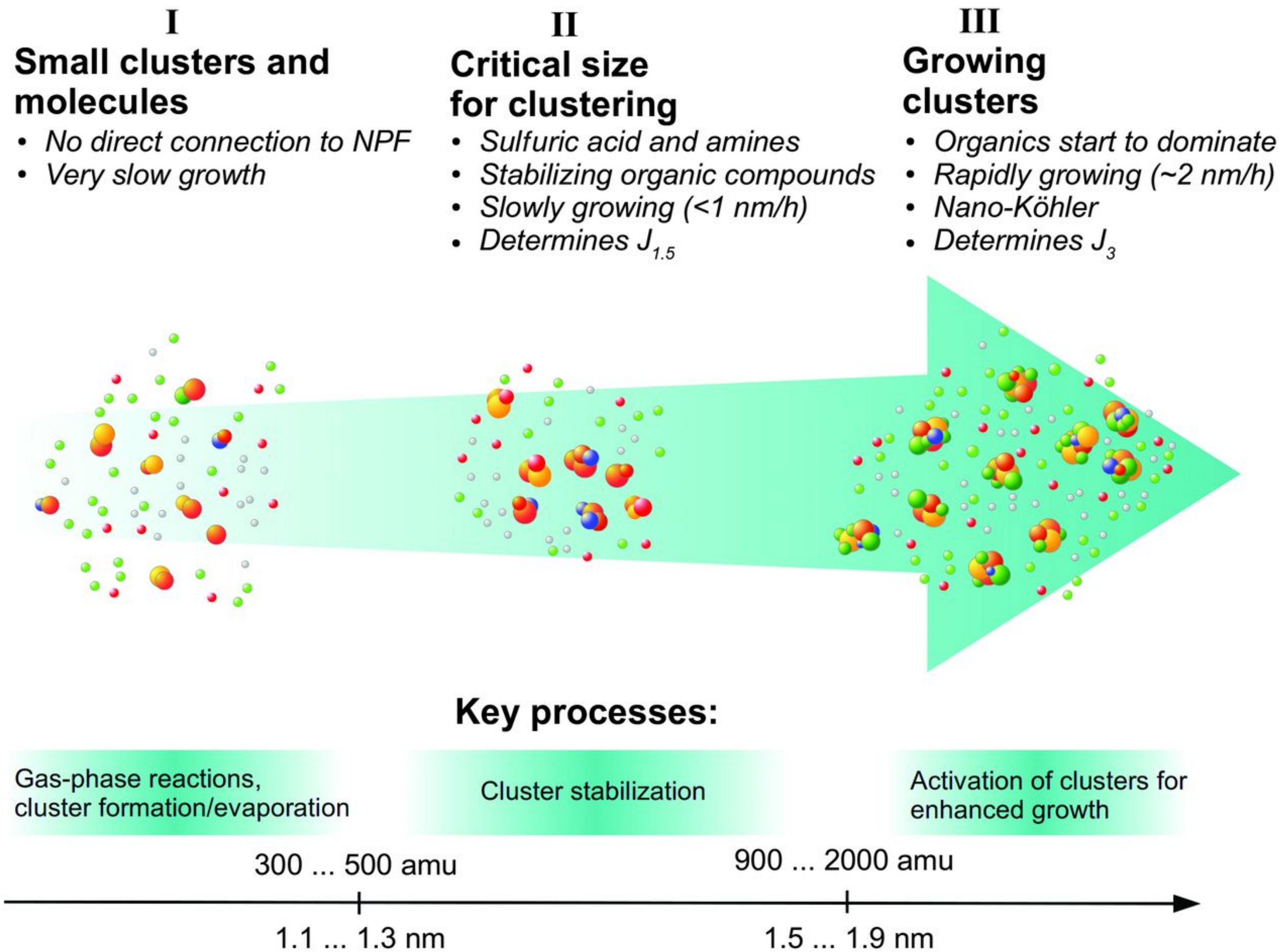
However, small “clusters” of ice form. Large enough “local” ice clusters are stable against decay, and act as seeds for further crystal growth



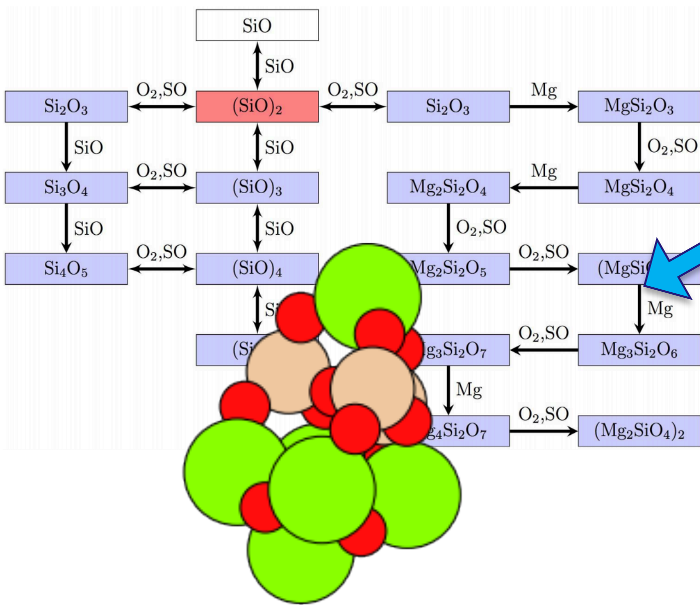
Moore & Molinaro, Nature 479, 2011

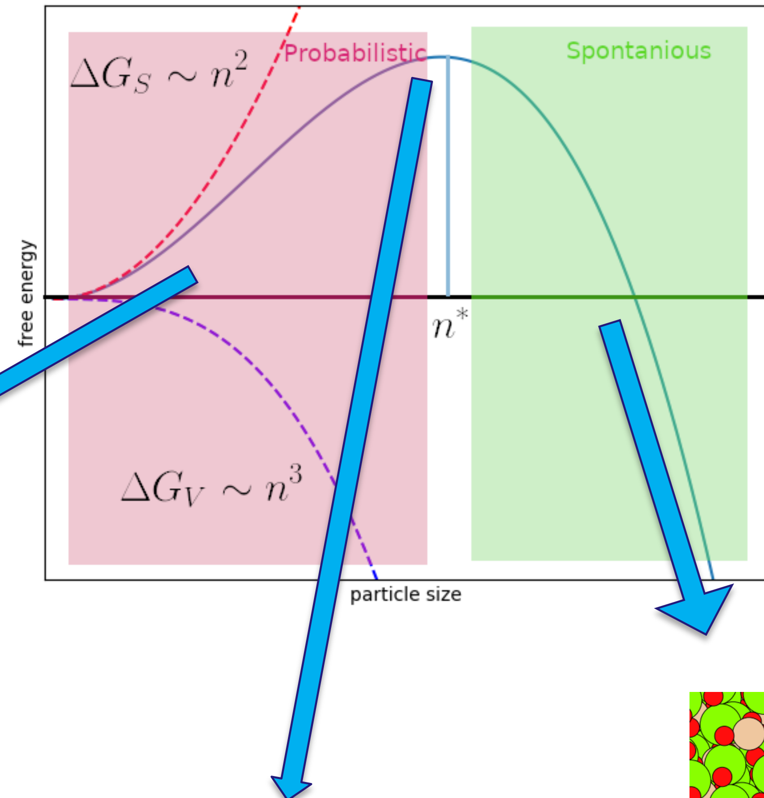
Pure water supercooled below the freezing point will remain liquid; crystal ice is thermodynamically preferred, but spontaneous bulk rearrangement is highly unlikely

Formation of growth of clusters from the vapor

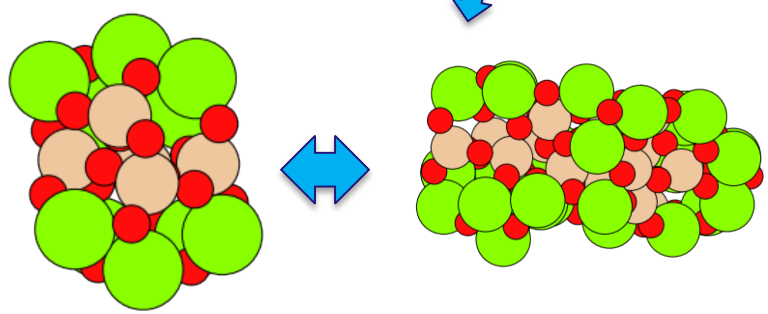


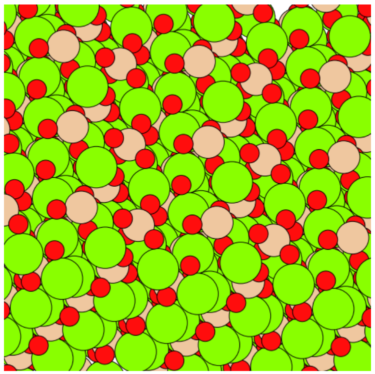
Nucleation



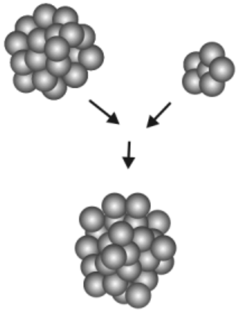


The formation rate of the critical size determines the efficiency of nucleation.





Surface chemistry



Small grains will condense and evaporate material, but after nucleation is completed growth is dominated by *coagulation*

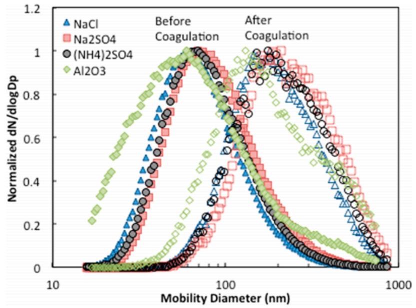
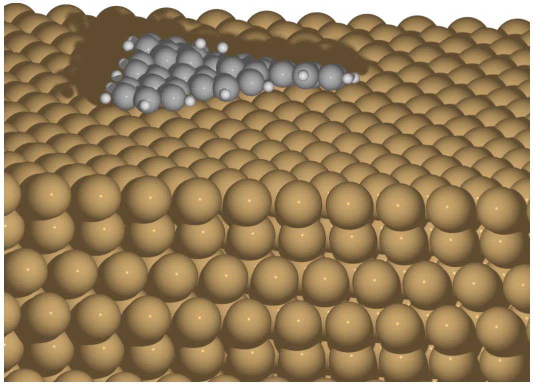


Figure 1. Size distribution of hygroscopic (NaCl, Na_2SO_4, $(NH_4)_2SO_4$) and nonhygroscopic (Al_2O_3) particles before (solid symbols) and after (open symbols) coagulation.

Montgomery et al., Environmental Science & Technology, 2015



PAH C36H20 formation and partial adsorption on a Cu(111) slab

Large grain surfaces provide a site that lowers reaction activation energies and decreases energy barriers in formation pathways.

At high temperatures, sp^2 bonded PA(N)Hs will begin to form with $sp^{2<x<3}$ bonded cages (fullerenes)

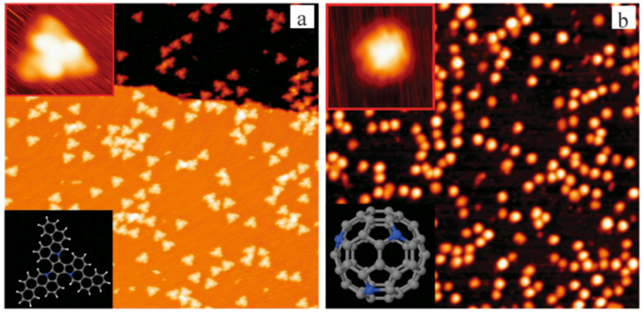


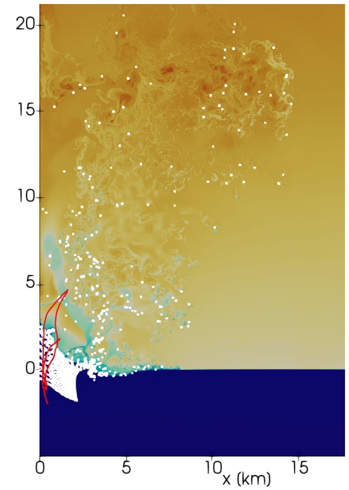
Fig. 8 STM images illustrating the surface catalyzed cyclodehydrogenation process. (a) The molecular precursor $C_{57}H_{33}N_3$ is deposited on the Pt(111) surface at room temperature. (b) After annealing up to 750 K triazafullerenes are formed. Scanned area is the same in both images.[43]

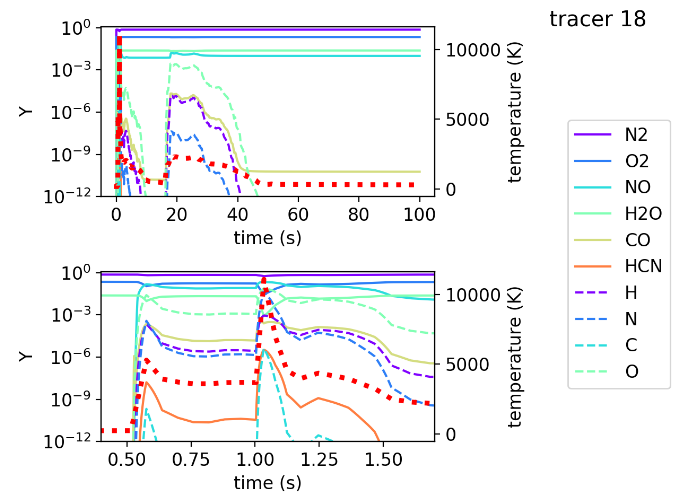
Méndez, Lópeza and Martín-Gago Chem. Soc. Rev., 2011, 40

Coupling to CASSIO

Tracers

Using tracers comoving with the fluid, we reconstruct the thermochemical environment in the flow and attach to it a reaction network

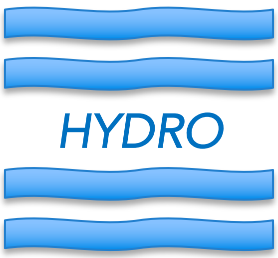




In-line (in development for Cassio)

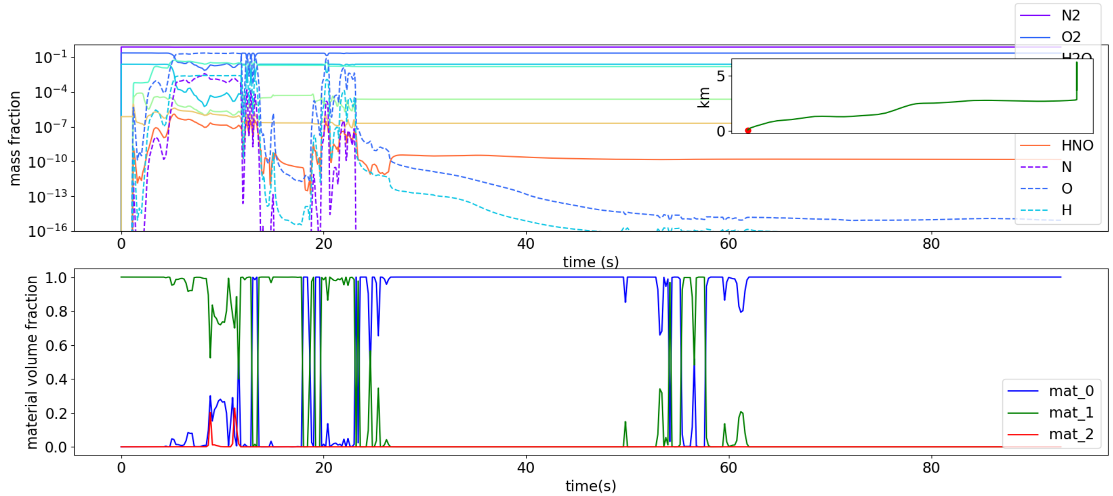
Use newly implemented/updated *passive-scalars* that represent number fields of molecules/dust bins. Operator-split reaction integration over the hydro time-step

```
pre_hydro()
use all, only: one
  $...$
  hdt = 0.5 * dt
  integrate_chemistry(t, t + hdt)
  $...$
end pre_hydro
```

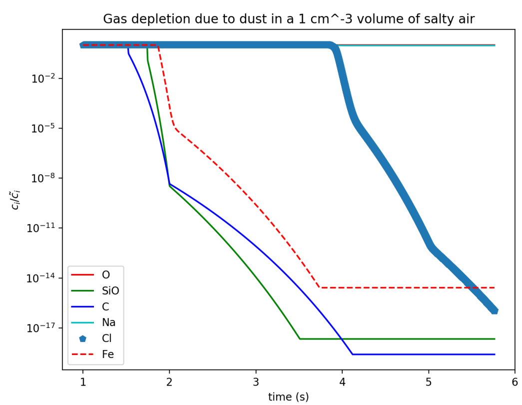


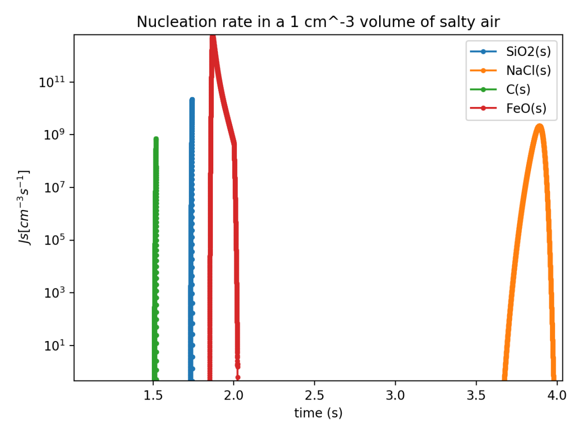

```
post_hydro()
use all, only: one
  $...$
  hdt = 0.5 * dt
  integrate_chemistry(t, t + hdt)
  $...$
end pre_hydro
```

Example Runs



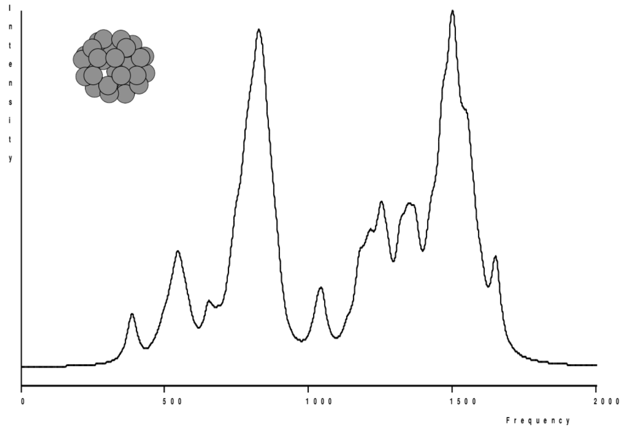
Chemistry on a tracer near an air/water interface undergoing shock-heating

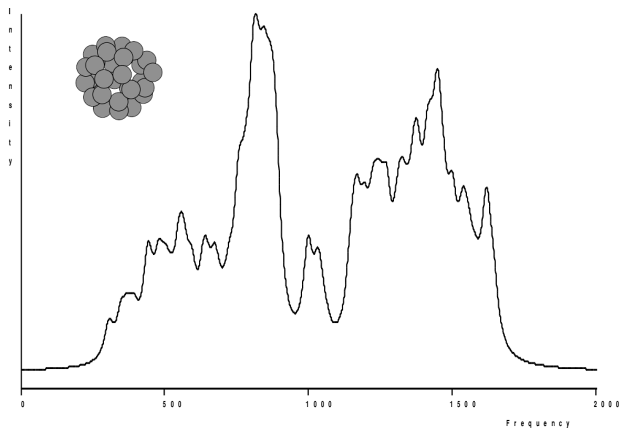




Gas phase number depletion due to dust formation, and nucleation rate of selected dust grains.

Observational spectrum





infrared spectrum of carbon grain clusters C32, C33

Unique chemical signatures can help determine key components of the event

Size and distribution of dust particles have different spectrographic signatures, and their spectra provide a probe of the fireball.

Infrared wavelengths can be found with linear response DFT, optical and higher-power spectra are available though TD-DFT.

Research outlook

Current goals

- Study the near-field chemical outcome of different fireball configurations and in different environments
- Determine the onset and extinguishing of nucleation, coagulation, and surface chemistry
- Expand model network to include important trace species (e.g. material from device)
- Composition and size distribution of refractory dust grains
- Generate useable inputs for medium- and long-term simulations

Future work

- Feedback from chemistry into hydro state
- Spectra/opacities for of significant molecule and dust species
- Integrate with Cassio materials to develop a scheme of matter transfer between phases

Thank you